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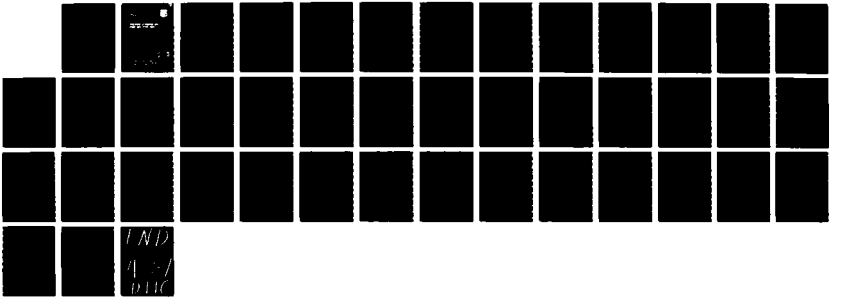

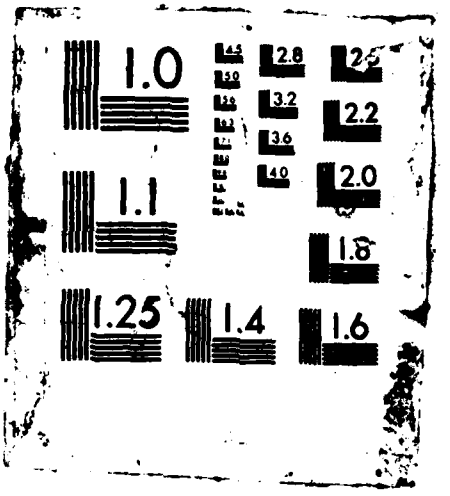
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Final Technical Report
November 1986

DEVELOPMENT OF RADIATION HARD GRADED INDEX OPTICAL FIBERS

EOTec Corporation

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The objective of this investigation is to reduce the optical fiber radiation sensitivity by doping with multivalent elements. Optical fibers, doped with arsenic under different redox conditions were prepared. Arsenic additions under slightly reducing conditions lowered the fiber radiation sensitivity, without influencing the intrinsic optical loss. This observation proved that arsenic can be used to improve optical fiber radiation hardening if optimized processing conditions are used. Further, development effort is needed to determine the effect of different parameters on radiation response. These parameters include, dopants and dopant levels, redox and fiber drawing conditions.

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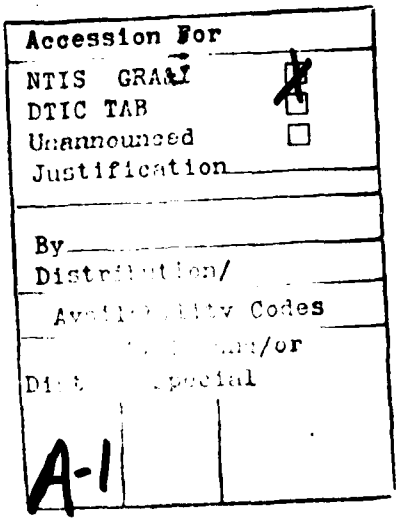

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1.0 OBJECTIVES

The objective of this program is to develop a radiation hard low loss graded index optical fiber. This fiber is to be used in high level pulsed or steady state radiation environments. To develop such fiber, the following specific objectives have to be achieved.

A. Identification of the type and nature of color center formation in the wavelength region of interest, i.e., 0.5-1.5 um range.

B. Identify the existing or new glass compositions which can be candidates for the radiation hard fiber core. The glass must be compatible with multivalent metal doping, and the required redox conditions during the preform manufacturing.

C. Explore dopants other than cerium and antimony which exhibit little or no contribution to the intrinsic optical absorption in the wavelength of fiber operation. Arsenic was chosen as a candidate dopant because it does exist in glass as As^{+5} and As^{+3} without the characteristic absorption band in the wavelength region of interest. In addition, arsenic is available in volatile compounds which are compatible with the modified chemical vapor process. The minimum effective level of doping will be explored.

These objectives constitute a basis for a systematic program to identify the nature of color center formation in optical fiber. Understanding the nature of the color center will define redox conditions required to suppress these color center formations during irradiation as well as provide quick transmission recovery.

2.0 IDENTIFICATION AND SIGNIFICANCE OF THE PROBLEM

The use of optical fiber systems offers significant advantages in a wide variety of military applications including airborne, ground based, and shipboard systems. Some of the advantages include: high bandwidth and long distance capabilities; small size and weight fiber and cable; elimination of ground loops, electrical isolation between interconnected modules; immunity to electromagnetic interference (EMI), radio frequency interference (RFI) and electromagnetic pulse; elimination of short circuit and spark hazards; and some measure of inherent transmission security.

While glass optical fibers are in effect immune to EMP from nuclear weapons, high optical loss can be induced from the associated radiation and, therefore, temporarily or permanently degrade the data transmission system. Radiation induced optical absorption and luminescence can cause such failures due to the increase of optical fiber loss or detector damage. Careful design and fabrication of optical fibers to reduce radiation effects can result in a fiber optic system capable of surviving many of the current nuclear threat environments and its multiplicity of kill mechanisms.

The radiation induced color center formation in low purity compound glasses had been extensively investigated under different radiation types and a range of doses. The introduction of cerium in two oxidation states (Ce^{3+}/Ce^{4+}) was found to reduce the radiation induced coloration. In the early developments of optical fibers, efforts were directed to improve the radiation resistance of plastic clad silica fiber and compound glass

fibers [6,7]. Later on, the radiation hardness of the doped silica fiber was pursued as its use in most commercial and military systems became mandatory. However, as of today, there is no doped silica fiber that meets the radiation hardness specification for most military systems. The objective of this program is to provide a systematic understanding of the different parameters influencing the radiation hardness and the development of a high bandwidth radiation hard fiber to meet the requirements of most system applications.

Under the effect of ionizing radiation, electrons (e^-) are freed and positive holes (h^+) are created in glass. This leads to color center formation as a result of positive hole and electron trapping on impurity and/or structural defect sites that may exist in the glass network[1-5, 8-11].

The most radiation hard fiber reported today is the pure silica core/polymer clad fiber made by Raychem[12]. This fiber was found to have a maximum radiation induced optical loss of 20 dB/km compared to 75 dB/km fibers previously produced by ITT. The improvement was due to the specific polymer selection at the core clad interface.

All glass fibers are superior to plastic clad silica (PCS) fiber in many respects. PCS fiber is rather difficult to terminate and available only in a low bandwidth step index configuration. Typically, they are higher loss than all glass fibers and show substantially higher losses at low temperature. To overcome some of the above mentioned difficulties, silica core/glass cladding fibers were explored.

High purity silica core with F^- or F^- and boron doped

cladding fibers were developed. As expected, radiation response of these fibers was similar to that of the plastic clad silica fibers. Better performance was reported for F^- and boron doped clad fiber as compared to F^- doped clad fibers.

The disadvantage of this step index fiber is the limited bandwidth and the relatively high transient radiation response. These limitations have been recognized for sometime; and efforts at Galileo and Corning Glass Works were aimed at producing radiation hard graded index fiber.

It is well known that multi-valent metal oxides such as cerium can reduce the radiation induced optical loss in borate and Silicate glasses[11,13,14]. Under the effect of ionizing radiation the following reactions take place:

$$As^{3+} + h\nu \longrightarrow As^{5+} + 2e^- \qquad (1)$$

$$As^{5+} + 2e^- \longrightarrow As^{3+} \qquad (2)$$

The new species will compete with the existing impurity and glass structural defects for the created electrons and positive holes: therefore, producing a reduced color center formation.

At Galileo[17], this approach for radiation hardening was explored. Graded index fibers having a SiO_2 $GeO_2 \cdot P_2O_5$ base composition were fabricated with OH^-, Sb and Ce doping. Some improvement in the radiation hardening of Sb doped fiber was found, while data on cerium doping were not conclusive. Recently, Ce was introduced during preform preparation in the form of a volatile non-halide organo-metallic compound utilizing the outside vapor deposition process (OVD)[15]. Doping with this volatile compound did not produce any deleterious effects of absorption beyond 850nm as compared to the undoped fiber. The

existence of Ce^{3+} and Ce^{4+} in the fiber was confirmed by UV measurement of its characteristic absorption bands. However, 0.4 wt. % was found to be the upper limit of cerium concentration before the core composition became unstable and crystallization initiated. This fiber was tested in Co^{60} irradiation up to 10^6 rads.silicon*. Initial results indicated 30% less radiation induced optical losses compared to the base glass(16). However, it showed a slow recovery.

We are convinced that radiation hard fibers which meet the strategic and tactical requirement of military systems can be developed by the appropriate doping of the fiber core and cladding. This hypothesis is confirmed by improvement in radiation hardening of arsenic doped fiber prepared during this contract. By studying and identifying the nature of color center formation in the wavelength of interest, optimizing the type and concentration of the multivalent metal oxide dopant, and optimizing the redox condition of the dopant and the base glass, the optical fiber radiation sensitivity can be reduced in terms of pulsed and steady state radiation environments.

* Standard unit of radiation absorbed dose in silicon.

3.0 PHASE I STATEMENT OF WORK

The objective of the program was to develop a radiation hard graded index fiber for utilization in radiation environments. Specifically, a base glass composition known to be the least radiation sensitive, is to be selected. An As^{3+}/As^{5+} mixture has to be introduced to the base glass under different redox conditions, and the resulting fiber response to radiation evaluated.

A. - Scope of Work

The work to be performed consisted of the following tasks:

1 - Identification of color center formation.

This task involves determination of the color center formation in the visible and near infrared range. This is to be achieved by studying the radiation response of optical fibers doped with multi-valent elements such as cerium which is prepared under different redox conditions. This experiment will differentiate between positive holes (h^+) and electron traps color center formation.

2 - Arsenic addition as a multi-valent element to the fiber.

The MCVD system is to be retrofitted for $AsCl_3$ doping.

3 - Effect of redox conditions.

The optimized As doped fiber is to be prepared under different redox conditions. The outcome of this task determines the optimum redox condition for minimum fiber response to radiation.

4 - Optical and radiation testing.

The testing includes measuring the fiber optical loss as

a function of wavelength before and after irradiation. The radiation induced loss will also be presented as a function of wavelength.

The induced optical loss at 0.82 micron will be monitored as a function of total radiation doses.

The electron spin resonance measurement is to be performed on some selected fiber samples before and after irradiation to characterize the type of color center formation in each fiber.

5 - Deliverable:

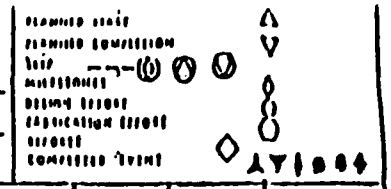
Several fiber samples are to be delivered to Hanscom Air Force base for radiation testing.

A final report is to be submitted to cover the experimentation results and conclusions.

The scheduled tasks and their completion dates are shown in figure 1.

FIGURE 1

PROGRAM SCHEDULE Development of Radiation Hard Graded Index Fiber/Phase1



TASK	OCT.	NOV.	DEC.	JAN.	FEB.	MAR.	APR.	MAY	(1986)
1. Identification of Color Center (Ce doping)	◆———	———	———	——▼					
2. Doping Additions As		◆———	———	———	——▼				
3. Effect of Redox Conditions			◆———	———	———	———	——▼		
4. Optical and Radiation Testing		◆———	———	———	———	———	———	——▼	
5. Deliverable Fiber (1km)				◆		◆			
Final Report								◆	

4.0 EXPERIMENTAL PROCEDURE

4.1 Preform Fabrication

Multimode step index preforms were made by the modified chemical vapor deposition (MCVD) process commonly used to make telecommunications grade optical fibers. This process involves depositing high purity silica glass compositions on the inside wall of a quartz substrate tube. The tube is then collapsed into a solid preform rod and elongated (drawn) into optical fiber. A schematic diagram of the MCVD system used in this program is shown in figure 2. The system is comprised of a chemical delivery system which uses electronically controlled mass flow controllers to precisely meter quantities of gases into a manifold. The manifold gases flow through a quartz substrate tube being held in a glassworking lathe. An oxyhydrogen torch is then traversed under controlled conditions along the substrate tube and externally heats the tube to cause high temperature oxidation of $SiCl_4$ and other dopant halides. The oxides form into small glassy particles and deposit in soot form downstream from the gas flow. As the torch passes over the soot, it consolidates into a high optical quality glass film. The refractive index profile of the preform is achieved by varying the dopant level of the reagent vapors over numerous glass deposition cycles. After glass deposition, the composite glass tube is heated and collapsed into a solid glass preform rod.

For this program, the gas delivery system was modified and expanded to incorporate a liquid $AsCl_3$ source bubbler and a CO/CO_2 gas manifold to control the redox condition during glass

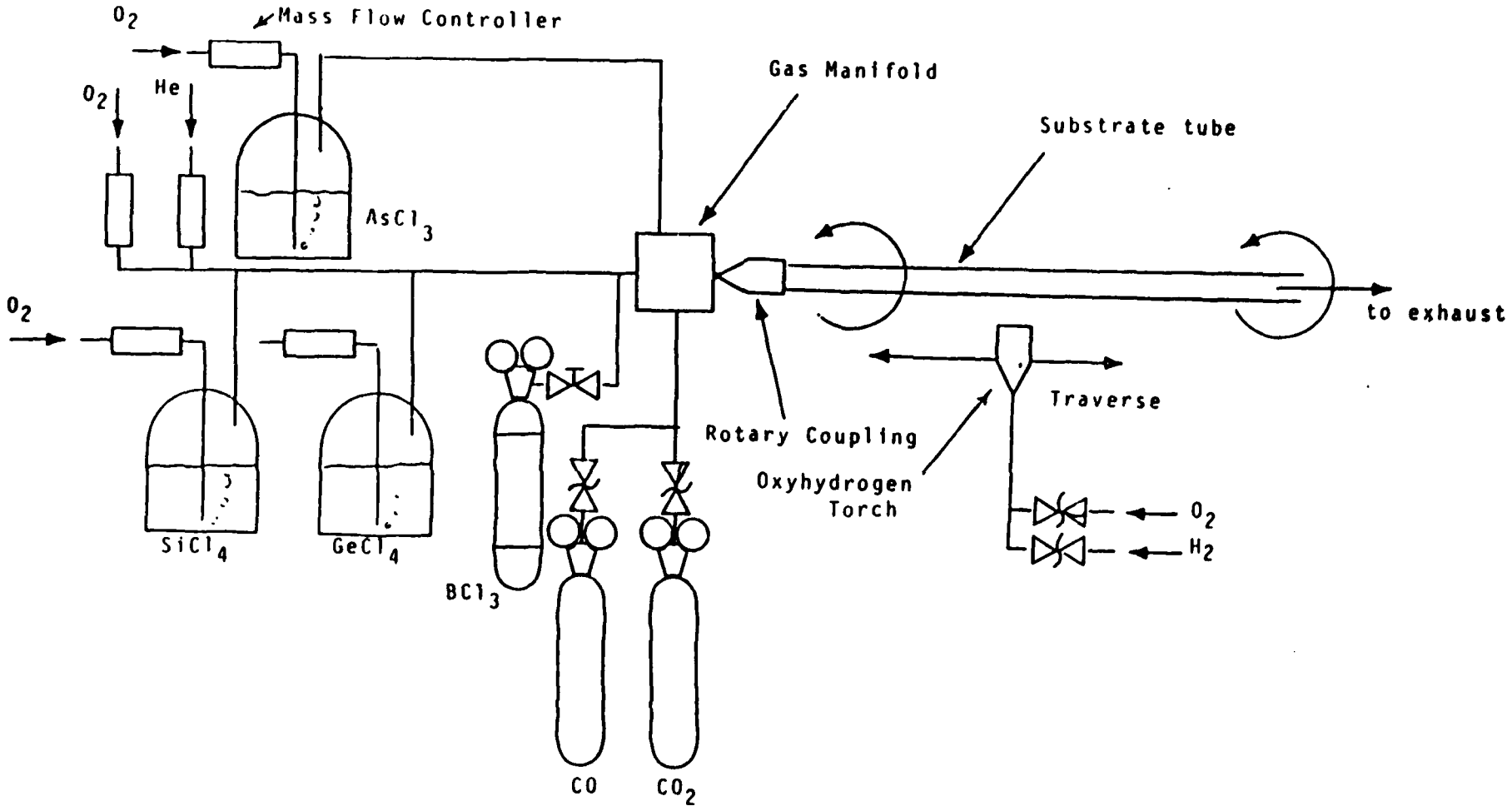


Figure 2. Schematic Diagram of MCVD System

deposition. $AsCl_3$ was chosen for the arsenic dopant source because it is compatible with the other metal halides, commercially available in high purity form, and posseses reasonable vapor pressure to be used in the MCVD process.

In order to meet the technical objectives outlined in the Phase I work plan, the preform fabrication effort was organized into three major tasks:

1. Base glass development.
2. Cerium doped preform development.
3. Arsenic doped preform development.

A detailed description of these tasks and the experimental results are as follows.

4.1.1. Base Glass Development

As outlined in the Phase I proposal, the GeO_2 doped silica glass family was chosen for the core glass composition. The long term objective of this program is to develop graded index fiber; therefore, it is important to incorporate a high level of core dopant in order to grade the refractive index profile and achieve high bandwidth. A refractive index difference between core and cladding glass was targeted to achieve a fiber numerical aperture of 0.3. We chose to use a "W" refractive index profile in designing the waveguide because it will yield the proper refractive index difference between core and cladding while accommodating a good level of core dopant. The use of the "W" waveguide profile also allows for lower attenuation due to the lower dopant level requirement as compared to matched clad designs which exhibit higher Rayleigh scattering loss due to high dopant level.

A series of step index preforms were made with different core and cladding compositions. The preforms were drawn into 125 micron fibers and tested for optical attenuation and numerical aperture. The calculated core and cladding compositions expressed in mole percent and optical results are listed below in Table I.

Table I Core/Cladding Compositions

Preform #	Cladding Composition	Core Composition	NA	Attenuation @ 850 nm dB/km
1	78.7% $SiCl_4$ 13.2% BCl_3 8.1% BF_3	86.7% $SiCl_4$ 13.3% $GeCl_4$	0.15	4.2
2	78.7 $SiCl_4$ 21.3 BCl_3	80.2 $SiCl_4$ 19.8 $GeCl_4$	0.14	3.8
3	85.5 $SiCl_4$ 14.5 BCl_3	62% $SiCl_4$ 38% $GeCl_4$	0.24	4.1
4	83.0 $SiCl_4$ 17.0 BCl_3	60.4% $SiCl_4$ 39.6 $GeCl_4$	0.29	3.6

The preform glass compositions used in preform 4 were chosen because of its high numerical aperture, and low optical loss/high dopant ratio combination. All experimental preforms, both cerium and arsenic doped, use these glass compositions as the host glass. The processing parameters used to yield repeatable 50/125 fiber preforms for experimentation followed the procedure described below.

A 17mm I.D. X 20mm O.D. by 65 cm long General Electric 982

WG waveguide substrate tube was mounted to a quartz inlet tube and etched for 30 minutes in a 50/50 mixture of HF/HNO_3. The tube is rinsed with de-ionized water and high purity methanol. The tube was then mounted on a glass lathe and connected to a rotary coupling.

Dry nitrogen gas was passed through the tube from the manifold. A teflon filter was held in the rotary coupling to ensure cleanliness of the coupling. An exhaust tube was then connected to the substrate tube and the gas system was switched to oxygen purge. The substrate tube was then fire polished at 1820° C under low pressure using dry oxygen gas for pressurization. This fire polishing step insured the high strength character of fiber drawn from the preform.

A combination heat-up and barrier layer deposition step was then performed. The gas system delivered vapors of oxygen, helium, $SiCl_4$, and BCl_3 with the same gas flow rates as the cladding glass with an excess of oxygen to create a high temperature deposition. The barrier layer was then deposited in two deposition passes. This heatup/barrier step brought the tube to a uniform warm temperature for an even cladding deposition and aids in preventing contaminants in the substrate glass from migrating into the deposited glass.

Immediately following the heat-up/barrier step, the cladding was deposited. The cladding was deposited in twenty deposition cycles at 1460 °C. The temperature was monitored and controlled by an optical pyrometer/proportional control system, which uses mass flow controllers to control the flow rate of the torch gases. The actual flow rate of reaction atmosphere gases during

cladding deposition were 1350 cc/min oxygen and 1000cc/min helium.

The preform core was deposited in twenty deposition passes at 1580 °C. 1350 cc/min oxygen, and 1000cc/min helium were used during core deposition. Both core and cladding were deposited with a deposition traverse speed of 1.9 mm/sec. The tube is then heated to 1900 °C and collapsed into solid preform rod. The experimental preforms fabricated in this program followed this procedure except for the addition of small amounts of cerium or arsenic dopant and the addition of CO or CO_2 to adjust the redox condition of deposition.

4.1.2 Cerium Doped Preform Development.

The incorporation 0.01-0.1% multivalent cerium as a dopant in the host glass was outlined in the Phase I statement of work. The use of an organo-metallic form of cerium was to be used as the dopant source. After a comprehensive literature search it was found that complexes of cerium, namely 2,2,7-trimethyl-3,5-octanedione used by Thompson[15] in the outside vapor deposition process were incompatible with the other metal halides of the MCVD system. In order to put cerium ion into the vapor stream, a closed melt crucible with a helium purge was assembled to melt $CeCl_3$ in an inert atmosphere and transfer the cerium into the vapor stream via the helium line . The results of a preform experiment using this setup for cerium core doping showed the cerium oxidizing into refractory particulates that formed entrained gas bubbles which caused catastrophic thermal fracture during the collapsing step of the preform processing. Two additional preform trials utilizing this technique were tried with similar results. The doping concept was then changed to vaporize the

$CeCl_3$ at the vapor stream. This technique has been used successfully at EOTec for doping terbium into silica glass compositions. A schematic diagram of the technique is shown in figure 3. A quartz inlet tube was modified to include a vaporizing chamber.

The cerium dopant was prepared by heating $CeCl_3$ under inert helium atmosphere in the vaporizing chamber to 1750 °C where it melted and wetted out the inside of the chamber. This formed a solid layer inside the chamber upon cooling. The preform substrate tube was then connected to the chamber and fire polished. The cladding was deposited and during core deposition the chamber was heated to 1750 °C where the $CeCl_3$ becomes volatile. Introducing inert helium gas into the chamber prevented the $CeCl_3$ from forming refractory CeO_2 (m.p. 2600 °C).

A preform employing this technique yielded a clean uniform transparent composite tube after deposition. However, upon the collapsing step, the preform fractured at the substrate to chamber junction most probably due to cerium oxide induced crystallization which increased thermal expansion mismatch upon cooling. Pieces of core glass were taken from the fractured preform and analyzed for CeO_2 with a scanning electron microprobe (SEM). Analysis showed the incorporation of 0.06% Ce. The results are encouraging, and additional Ce doped preform trials utilizing this technique are proposed in the work plan for Phase II.

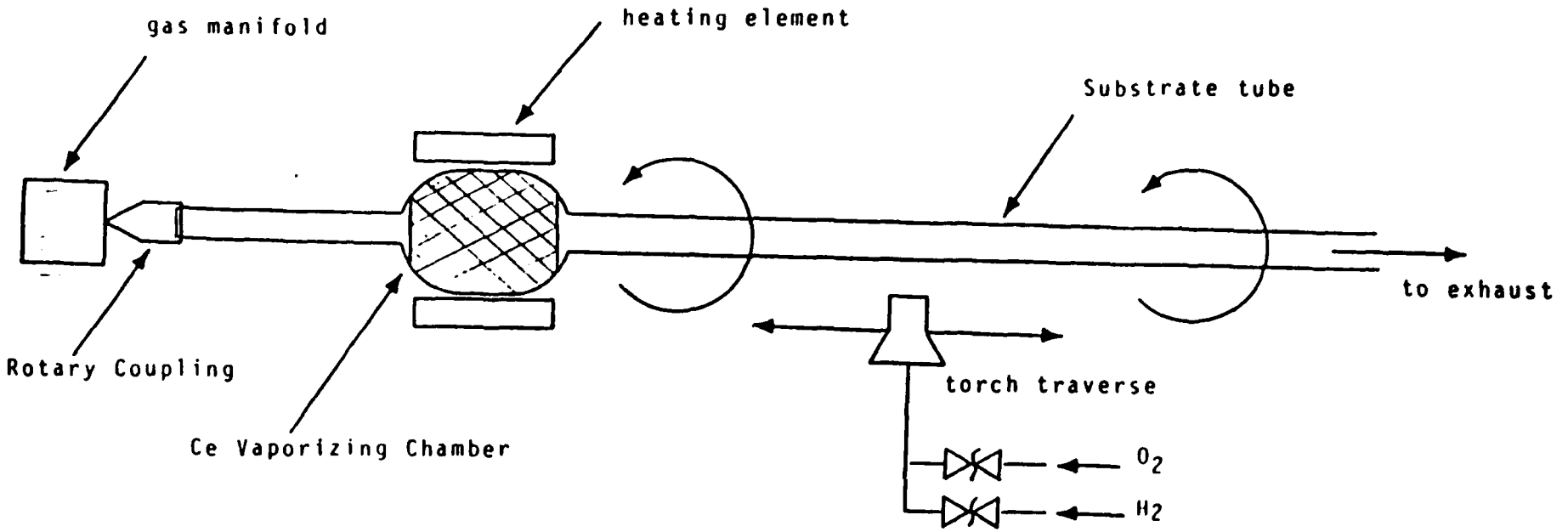


Figure 3. Schematic Diagram of Technique used to Dope Cerium in Preform.

4.1.3 Arsenic Doped Preform Development

As outlined in the Phase I statement of work, preforms with 0.01 to 0.1% arsenic were made under various oxidizing and reducing atmospheric conditions. Although the identification of color center formation species was to be determined by the cerium doped preform series, the same information can be derived from these arsenic dopant experiments.

An initial series of three preforms were fabricated. The first preform was doped with 0.1% $AsCl_3$ under standard host glass parameters. The other two were made with 0.1% $AsCl_3$ under intermediate, oxidizing and reducing atmospheric conditions respectively. The $AsCl_3$ used was high purity 99.9995% metals basis supplied by Alfa Products of Danvers Massachusetts. It was contained in a teflon lined stainless steel bubbler and vaporized into the gas manifold by passing oxygen carrier gas. The intermediate oxidizing atmosphere was created by introducing 600 cc/min of high purity 99.995% zero grade carbon dioxide into the gas manifold. The reducing atmosphere was achieved by introducing 600 cc/min of high purity 99.995% zero grade carbon monoxide into the gas manifold. Some brief observations and data on these preforms follow.

4.1.3.1 Arsenic Under Strong Oxidizing Atmosphere

The preform was processed according to the standard host glass parameters, and as described in the host glass section. The presence of a 1350 cc/min oxygen flow created an oxidizing atmosphere in this host glass composition. The $AsCl_3$ was introduced during the core deposition and the reaction zone

showed a slight orange discoloration as compared to normal. The core deposition also required a slightly high deposition temperature of 1600 °C. A slight change in composition was also indicated by the exhausted soot exhibiting a different, denser texture.

4.1.3.2 Arsenic Under Intermediate Oxidizing Atmosphere

The preform processed normally through cladding deposition. During core deposition, the deposition temperature deviated from a normal 1580 °C to over 1640 °C. The amount of deposited glass as determined by the final preform cross-section was less than standard, also indicating a change of composition requiring more reaction energy.

4.1.3.3 Arsenic Under Reducing Atmosphere

The preform was processed according to the standard host glass parameters. During the core deposition, the orange discoloration observed in the strong oxidizing atmosphere case was more prominent. The preform also ran at a slightly lower core deposition temperature of 1535°C which caused less preform deformation and shrinking.

These initial three preforms were drawn into 125 micron fiber and tested for radiation response. The results indicated the arsenic doped fiber under reducing (CO) atmosphere was superior to the others. A second series of preforms were fabricated with both increased and decreased levels of carbon monoxide in the gas stream to further study the optimum redox condition.

In the second reducing atmosphere experiment, As CO-II, the level of carbon monoxide was increased from 600 cc/min in the first

reducing experiment to 1000 cc/min. The preform core deposition temperature ran high at 1620 °C as compared to the standard core deposition temperature of 1580 °C.

In the third reducing atmosphere experiment, As/CO-III, the level of carbon monoxide was reduced from the 600 cc/min used in the first experiment to 300 cc/min. The preform ran at a lower core deposition temperature (1530 °C) than the standard deposition temperature, very similar to the first experiment.

4.2 Fiber Drawing:

Fibers were drawn using a graphite resistance furnace under argon atmosphere. The preform diameter was typically 11 mm and was drawn into 125 micron fiber at a speed of 35 meters/min. A high index silicone coating was applied in-line to the fiber surface and thermally cured before it contacted a belt wrap drawing mechanism. An outer jacket of Hytrel® was also applied in line to a diameter of 400 microns. Approximately 500 meters of fiber was drawn from each preform.

4.3 Pre-Irradiation Characterization

4.3.1. Optical Attenuation

Optical attenuation is determined by the cut back technique. Each length is excited with steady-state mode distribution. Fibers are injected at the steady-state numerical aperture with a 1000 W tungsten-halogen source and a stabilized power supply. The optical attenuation is measured between 0.4 and 1.1 micron using interference filters. The output power is detected with a silicone photodiode coupled to a lock-in amplifier. Measurement of the two lengths is done with the input end common to both lengths; therefore avoiding errors resulting from differing launch conditions.

4.3.2 Numerical Aperture

The effective numerical aperture of the fiber was measured by scanning the far field radiation pattern. The output of the detector was plotted as a function of its off fiber axis angle as it sweeps the far field pattern. The effective NA is defined as the sine of the half angle which includes 90% of the power emitted from a fiber longer than the steady-state length.

4.3.3 Fiber Strength

All fibers were proof tested at a 50kpsi level using a Sterling Davis proof tester model #F.TESFP.

4.4 Post-Irradiation Measruements

4.4.1 Radiation Response Testing

The in-situ measurements of the radiation induced coloration were carried out by RADC personnel on their Co^{60} gamma irradiation facility. In the first experiment, fibers were irradiated at a dose rate of 340 rads/min at 25 °C. In the second experiment, the fiber samples were irradiated at 473 rads/min.

The optical loss was measured at 0.85 micron for all fiber samples and the induced loss was plotted as a function of cumulative dose.

Fifty meters of the fiber was spooled into a coil and placed in a predetermined position inside the Co^{60} source hot cell. The fiber leads were fed through the hot cell and connected to an LED and a silicone detector respectively. The detector output was monitored as a function of the cumulative dose. The actual absorbed (gamma) radiation dose was measured using thermoluminescent dosimeters (TLD'S) placed in quadrature

around the fiber reel and in line with fiber position.

4.4.2 Electron-Spin-Resonance

The electron-spin resonance (ESR) spectroscopy was performed at the Naval Research Lab, Washington, D.C. The defect centers were characterized after irradiating the optical preform sample with x-ray at cryogenic temperature and monitoring the (ESR) spectrum as the sample warmed up to room temperature.

To avoid the signal noise due to the low purity quartz T-08 jacket, the optical preforms were etched out completely with concentrated hydrofluoric acid.

5.0 RESULTS

5.1 PreIrradiation Measurements:

The spectral attenuations of the first fiber series are shown in figure 4. This series consists of a germanium silicate base glass (Figure 4 curve D), base glass doped with 0.1% As under O_2 atmosphere (Curve C), As doped glass under CO_2 atmosphere (Curve B) and As doped glass under CO atmosphere (Curve A). For most of the spectral range, the base glass composition shows the lowest optical attenuation. The addition of As to the base glass increases its attenuation in the visible range. Addition of CO_2 to the gas mixture generally increases the optical attenuation, particularly in the infrared region (curve B). The addition of the more reducing CO atmosphere is especiallly interesting. While there is no noticable effect on the attenuation in the infrared region (curve A) the visible part of the spectrum increases significantly. Furthermore, there is a pronounced absorption band around 680 nm.

To further explore the effects of a reducing (CO) atmosphere, higher and lower CO/O_2 mixtures were used to prepare optical fibers . The spectral attenuation of these fibers are shown in figure 5, along with that of the base glass fiber for comparison. The addition of lower CO/O_2 ratio increases the intrinsic attenuation (figure 5 curve B). It is interesting to note the absence of the 680 nm band. Furthermore, increases in the CO/O_2 ratio raised the attenuation level (figure 5 graph A) . Once again, the 680 nm band is visible and the high absorption at 950 nm indicative of high OH content in the fiber is evident.

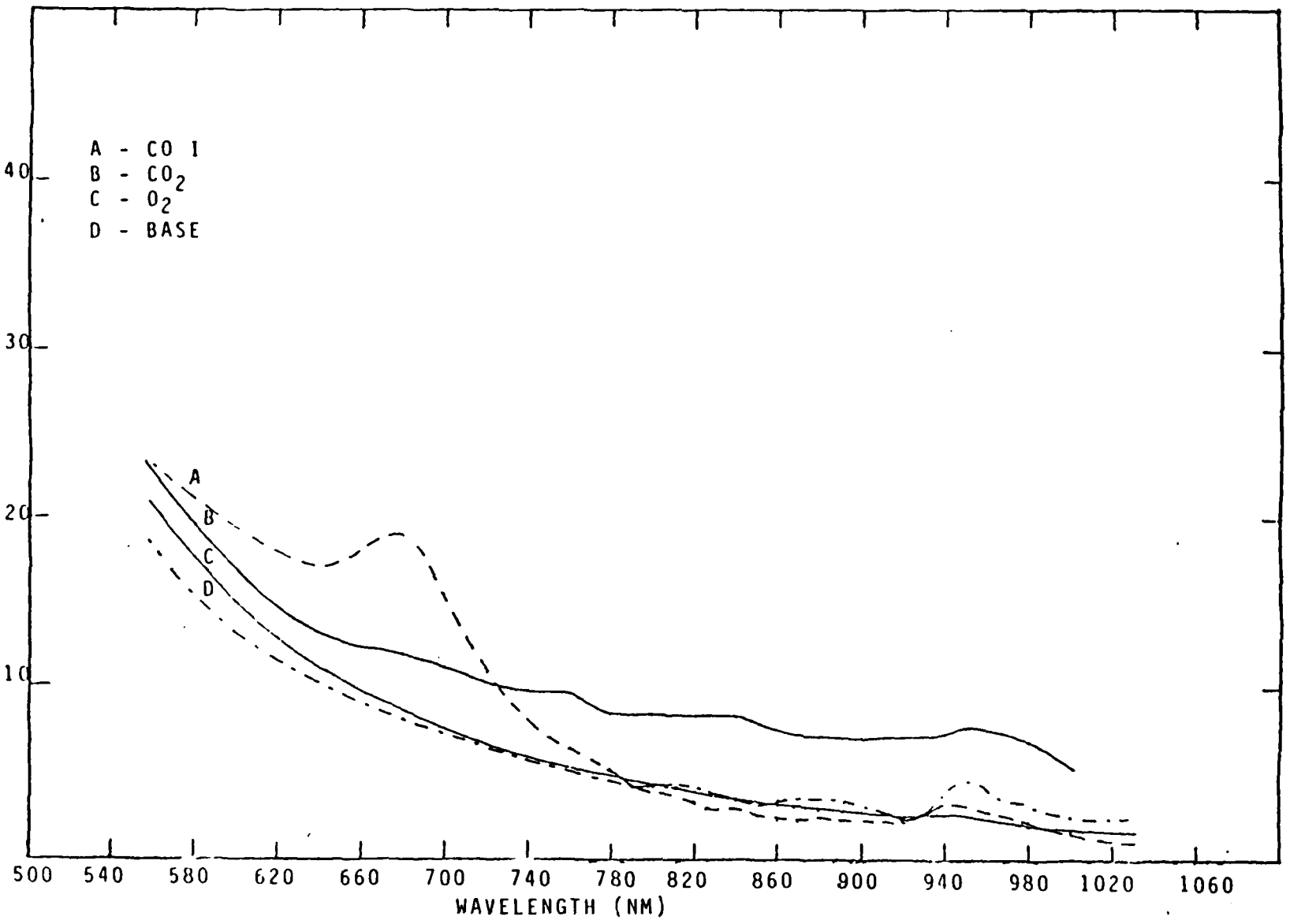


Figure 4. Effect of the redox condition on the intrinsic spectral attenuation of As doped germanium silcate optical fibers.

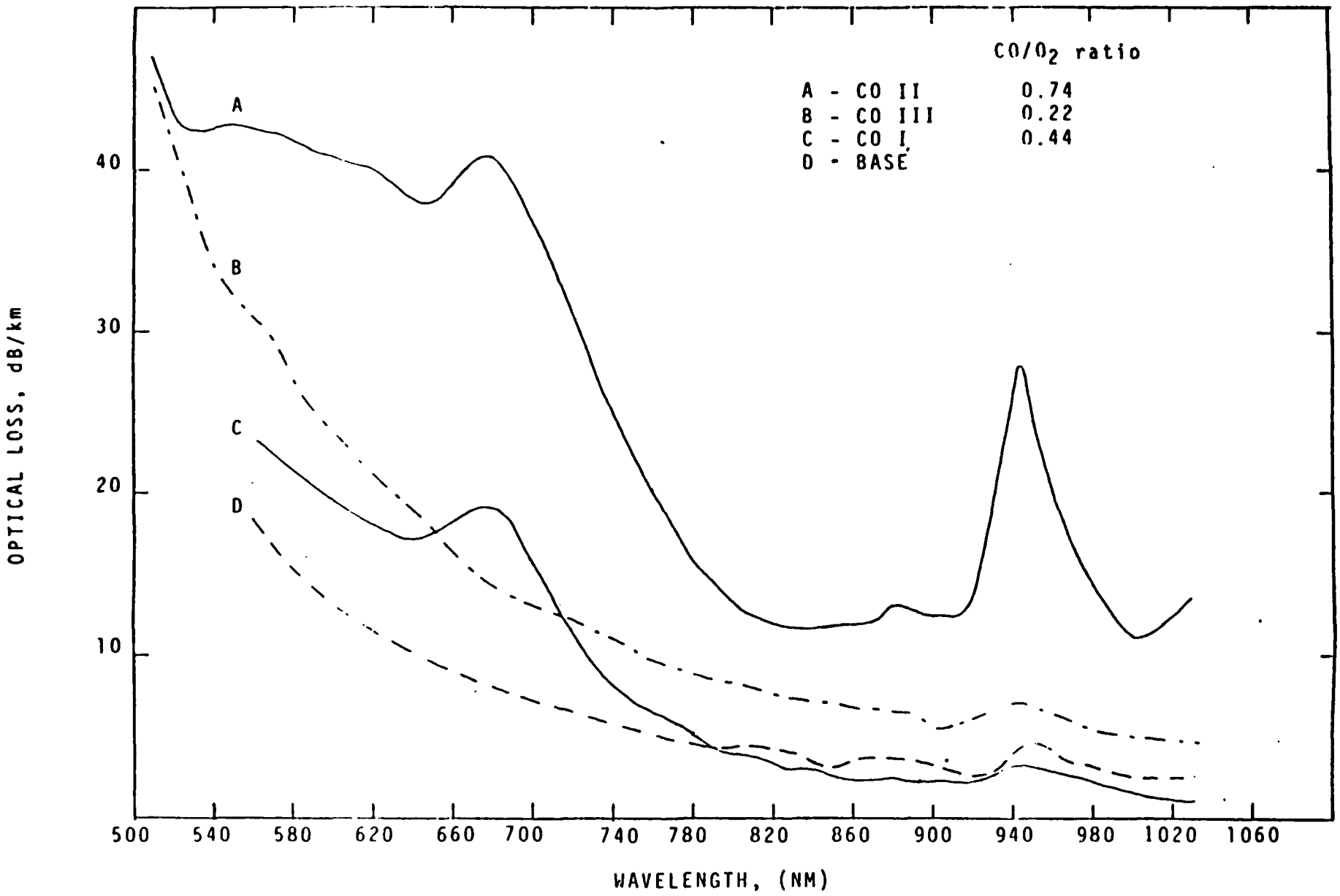


Figure 5. Effect of CO/O_2 ratio on the intrinsic spectral attenuation of arsenic doped germanium silcate optical fibers.

5.2 Irradiation Measurements

The effect of the redox condition on the radiation response of arsenic doped fiber was determined and compared with that of the base glass fiber. This effect was studied as a function of the cumulative radiation response at 0.85 micron and is presented in figure 6. As shown in figure 6, the addition of As to the base glass considerably increases its radiation response, however, by changing the redox conditions from oxidizing (figure 6 curve A) to reducing (Figure 6 curve D) the radiation response is substantially reduced to even lower levels than that for the base glass fiber. CO_2 atmosphere has an intermediate redox effect compared to O_2 and CO. The radiation response associated with CO_2 as expected has a value between those of O_2 and CO treated fibers.

As it was suggested in the phase I proposal, it is essential to have an optimum As^{3+}/As^{5+} ratio to suppress the color center formation. The addition of CO to the reacting gas mixture supports this suggestion.

To study the effect of CO addition in some detail, the radiation response of As doped fiber prepared under different CO/O_2 ratios were investigated. The CO/O_2 values are listed in figure 5. As shown in figure 7 curves A and C , low and high CO/O_2 ratio respectively, increase the radiation response. A 0.44 CO/O_2 ratio resulted in the lowest radiation response reported in this program as shown in figure 7 (curve D).

The effect of the CO/O_2 ratio on the radiation induced optical loss of the tested fiber measured at 0.85 micron and total dose after 1.8×10^4 rads is shown in figure 8. Again the data shows clearly the reduction of the radiation induced

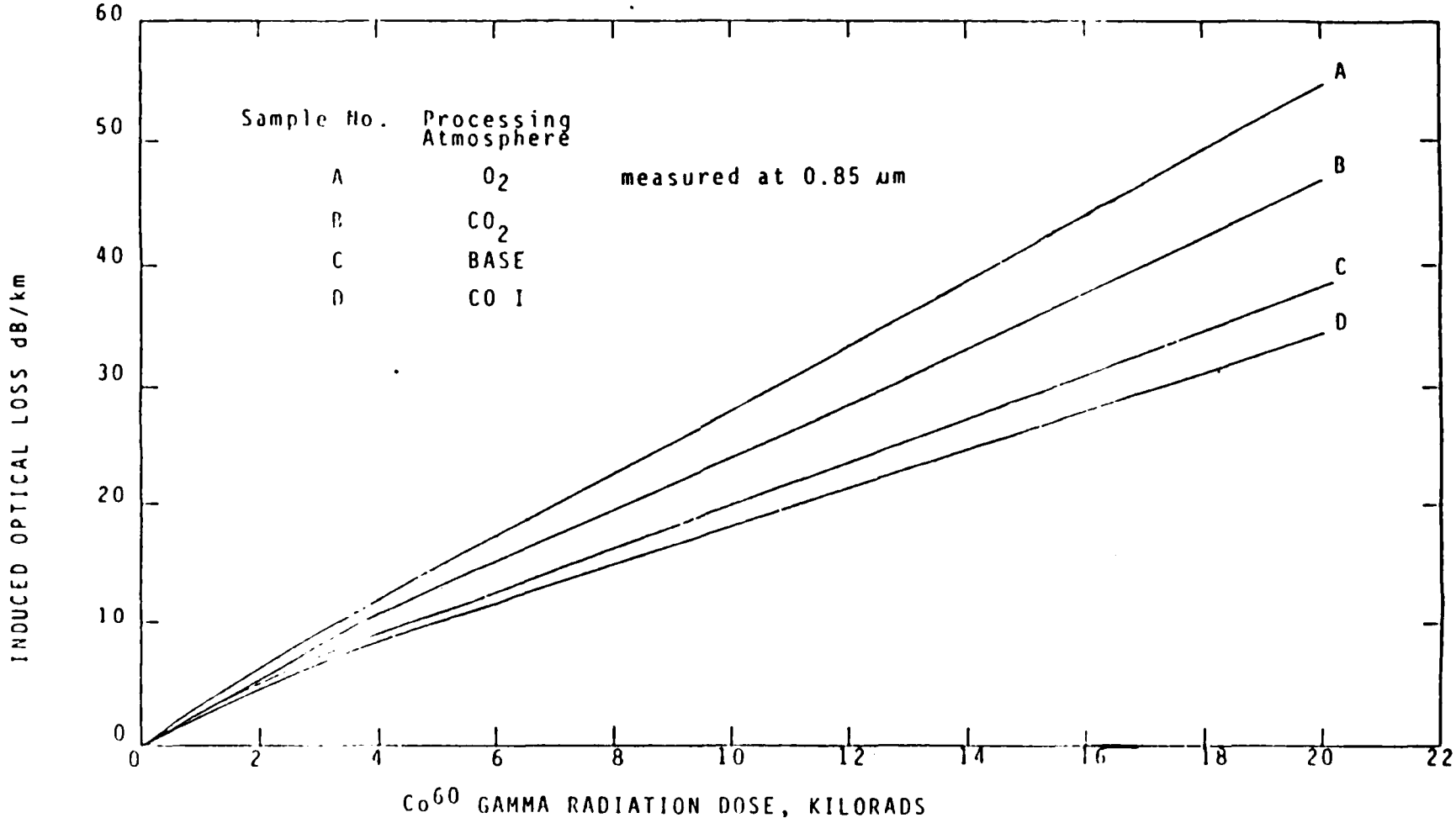


Figure 6. Effect of the Redox Condition on the radiation response of arsenic doped germanium silcate optical fibers.

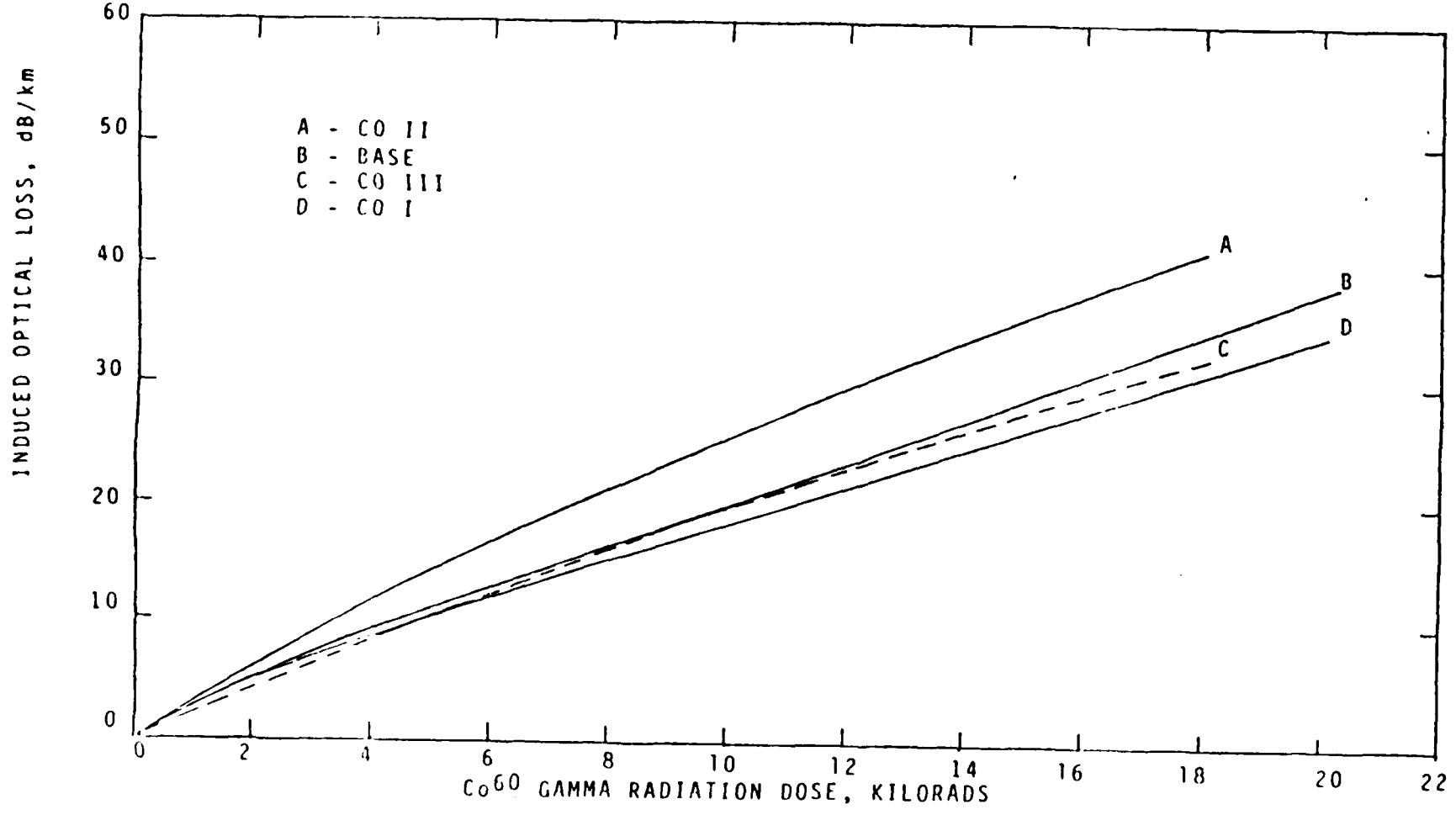


Figure 7. Effect of CO/O_2 ratio on the radiation response of arsenic doped germanium silcate optical fibers.

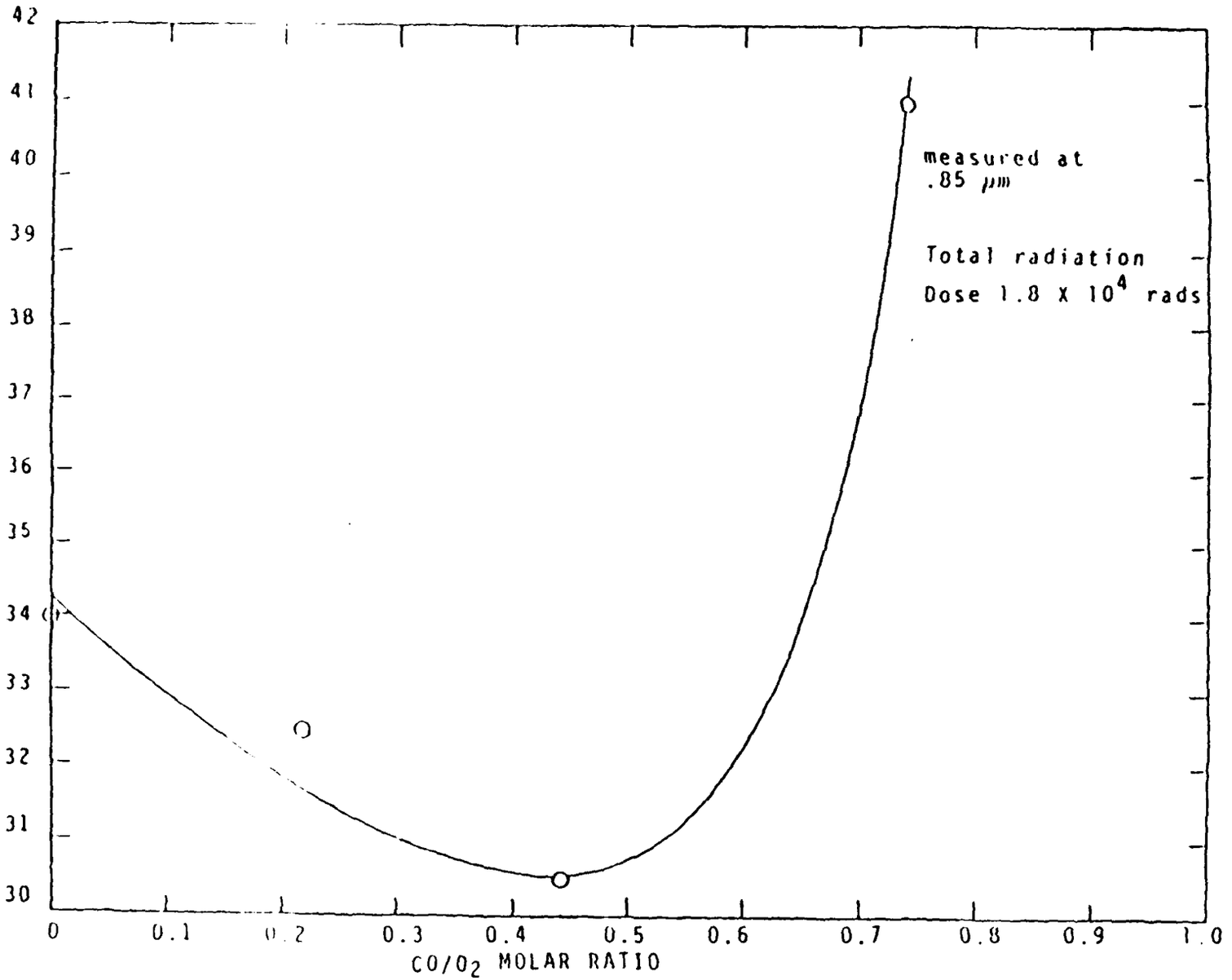


Figure 8. Effect CO/O_2 ratio on the radiation induced optical loss of Arsenic doped germanium silicate optical fibers.

response reaching a minimum between 0.4 and 0.5 CO/O_2 ratio. Further additions of CO increase the fiber radiation response. Due to the limited number of experiments, the exact optimum condition can not be determined. More experiments are needed to determine this optimum redox condition and its relationship to the arsenic doping level.

The spectral attenuation was measured on all the samples a few weeks after irradiation to study the effect of redox conditions on the permanent radiation induced damage. As shown in figure 9, arsenic doped fiber under an O_2 atmosphere had the highest permanent damage while similar fiber doped under a CO atmosphere exhibited the least damage. The intermediate redox condition with CO_2 shows a moderate increase in the induced optical loss compared to that of the reducing condition. This observation holds true over the entire range of measurements.

A study of the types of color center formation was attempted by thermal bleaching of the irradiated optical fiber. This study should give indications on the relative stability of the different color centers formed. Irradiated fibers were heated up to 150 °C. No detectable decrease in the radiation induced optical loss was measured. The Hytrel upper service temperature limited the heating beyond 150 °C.

Similar conclusions can be extracted from thermal bleaching of the irradiated optical preform, which is monitored by the electron spin resonance of different color centers as a function of treatment temperature. There is no limitation, in this case, on the treatment temperature as no organic coating is used.

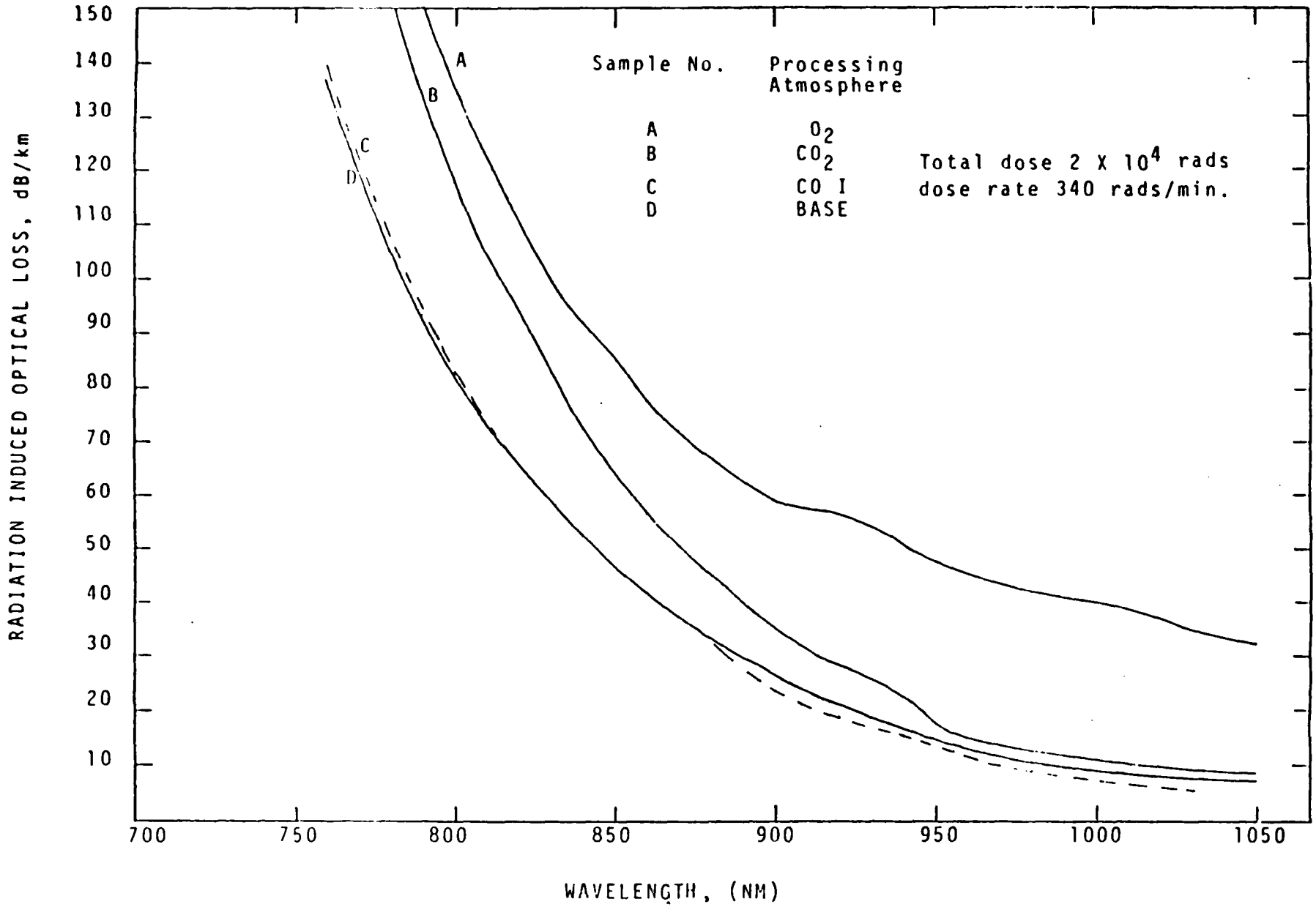


Figure 9. Effect of redox condition on the radiation induced spectral attenuation of arsenic doped germanium.

6.0 DISCUSSION AND CONCLUSIONS

Preparation of optical preform under reducing atmoshpere increases the intrinsic optical absorption in the visible spectral range. However, there is no significant increase in the optical loss in the infrared region. As reducing atmosphere lowers the fiber response, it would be interesting to establish a correlation between the intrinsic defect center created in the visible region and the reduction in radiation response. Jackson et al [18] reported similar observation where the reducing conditions increased the 245nm absorption band in germanium silicate glasses.

The radiation response data showed that doping optical fiber with arsenic under slightly reducing atmosphere (CO/O_2) lowers its radiation sensitivity. These results are encouraging; however, further work is needed to determine the optimum dopant concentration and optimum redox and drawing conditions. Preliminary data on the effect of redox conditions indicate that the absorption in the 0.85 um region is mostly due to positive hole center formation.

In conclusion, it has been proven that arsenic can be used to reduce the optical fiber radiation response, if optimized redox conditions are used. Further development effort is needed to determine the effect of different parameters on the fiber radiation response. These parameters include, dopants and dopant levels, redox and fiber drawing conditions.

7.0 RECOMMENDATIONS FOR FURTHER RESEARCH

Based on the information obtained during the Phase I effort, the following tasks are recommended for further improvement of

the optical fiber radiation hardness.

1. Study the effect of Arsenic doping level in different glass systems and select the optimum arsenic level.

2. Study the effect of redox conditions in more detail to determine the proper gas mix which would lead to the lowest radiation response. The effect of the redox conditions on the As^{+3}/As^{+5} should be investigated and the ratio should be determined analytically.

3. Effect of redox condition on the base glass composition. In phase I, only the effect on the arsenic doped glasses was investigated. This proposed investigation will simplify the study and the analysis of the redox effect on the intrinsic structural defect formation, without the complication from the multivalent element additions.

4. Explore other dopants such as Ce and Sb using the new outside vapor deposition technique (OVD) for doping rare earth compounds developed at EOTec. This technique was used at EOTec to fabricate Terbium doped optical fibers. This technique is very interesting, as it is possible to control the redox condition during the preform sintering stage.

5. Study the effect of fiber drawing condition on the radiation response of the doped fiber. The study should include drawing temperature, speed and atmosphere.

6. Optical and Electron Spin Resonance (ESR) analysis of the different E' and other color center formation should be used in characterization . Thermal bleaching can be used to determine the relative stability of each defect type.

7. Study the effect of new glass compositions, such as $Al_2O_3 \cdot P_2O_5$, on the intrinsic defect formation. These dopants (Al_2O_3, P_2O_5) can be added to increase the silica refractive index while maintaining Al_2O_3/P_2O_5 ratio equals one. This will reduce the concentration of intrinsic structural defects. Furthermore, these oxides are more stable and can withstand more severe redox conditions compared to germanium oxide.

8. Extend the investigation to 1.3 and 1.55 micron range. More systems are now operating at those wavelengths to take advantage of the lower optical loss. Radiation response is also lower at these wavelengths with the minimum around 1.3 micron.

9. Study the effect of cladding composition on the radiation hardness. Boron doped, boron and fluorine doped and fluorine doped cladding compositons should be investigated.

10. The effect of composition profiles on the the radiation response should be studied.

The development of this radiation hard fiber will have extensive military and industrial applications. The following are some examples:

A. We would anticipate applications for process control and automation, local area networking, and general use in the nuclear utility industry and in the nuclear medical market place.

B. Federal government usage would be imperative for continued data, video, and audio communication and control between various military platform and command center operations and weapon delivery systems which can survive in the event of nuclear attack.

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